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(71) Applicant: RADIANT TECHNOLOGIES, INC. [US/US]; 1009 Bradbury Drive, S.E., Albuquerque, NM 87106 (US).

(72) Inventors: BULLINGTON, Jeff ; 5633 Wheelwright Avenue, N.W., Albuquerque, NM 87120 (US). ELLIS, Robert, V. ; 700 Paseo Del Mar, N.E., Albuquerque, NM 87123 (US). WALKER, Richard, T. ; 3307 S.E. Linda Vista Drive, Albuquerque, NM 87106 (US).

(74) Agents: WARD, Calvin, B. et al.; McCubbrey, Bartels, Meyer & Ward, Suite 2700, One Post Street, San Francisco, CA 94104-5231 (US).

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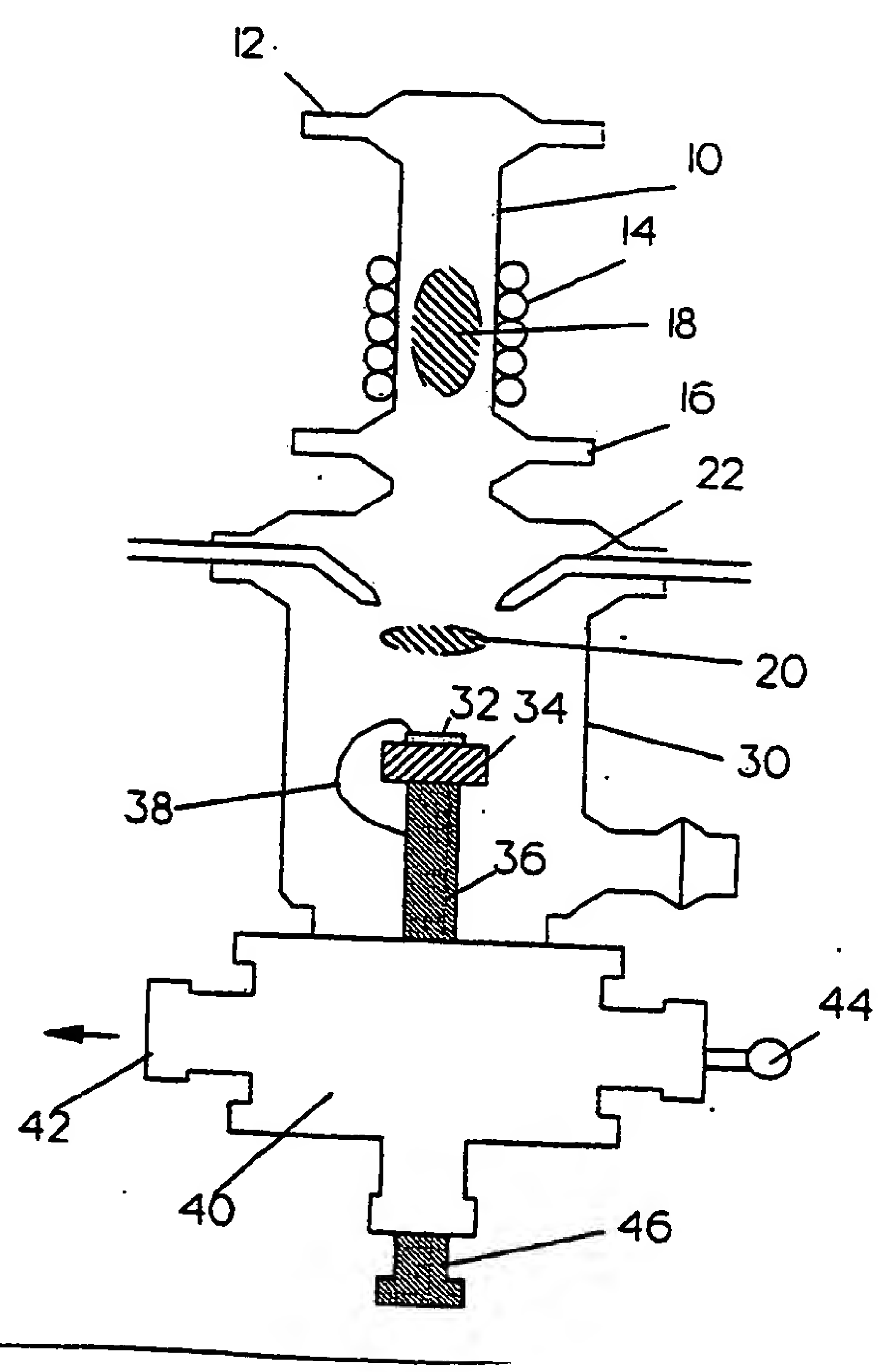
(54) Title: METHOD FOR DEPOSITING A THIN FILM ON A SEMICONDUCTOR CIRCUIT

(57) Abstract

A method for coating the surface of a substrate with a thin film of ferroelectric material. A flow of a metalorganic vapor such as tetraethyl lead, zirconium t-butoxide, and titanium isopropoxide is directed towards a silicon substrate. Also, a flow of ionized particles is generated by subjecting a gas to an rf electromagnetic field. The afterglow of excited state species particles intersects the path of the flow of metalorganic vapor at a location displaced from the surface of the substrate producing a flow of activated metalorganic vapor which then deposits on the heated substrate. The figure illustrates a plasma enhanced chemical vapor deposition reactor which consists of a plasma generator (10) where the excited species is generated, a precursor activation chamber (20), the deposition region where the heated substrate (32) is located, and an exhaust system (40).



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METHOD FOR DEPOSITING A THIN FILM ON A SEMICONDUCTOR CIRCUIT

Field of the Invention

The present invention relates to methods for depositing thin film coatings, and more particularly to depositing ferroelectric thin film coatings onto the surface of substrates that cannot withstand high temperatures.

Background of the Invention

The silicon chip has become a symbol of modern electronics. Semiconductor-based devices dominate the digital electronic world, and new applications of such devices are continually being created. As these applications demand greater optimization, semiconductor devices are developed which are both smaller and faster than their predecessors. A single modern integrated circuit contains a multitude of distinct transistor and other semiconductor devices on a single piece of semiconductor material.

As this optimization process continues, the physical limits of existing semiconductor technology present barriers to continued miniaturization. One such barrier is created by the necessity of the use of capacitors in these semiconductor devices to store charge. For example, some digital memory devices typically require capacitors to retain the charge necessary to retain memory data intact. Dynamic RAMs, as such devices are called, must be refreshed periodically to prevent the data from being lost. The period of time required between such refreshes is important to computer hardware design, as more complex circuitry is required where the period is shorter.

Unfortunately, the period between required refreshed is dependent upon the capacitance of certain capacitors within the DRAM integrated circuit. Capacitance itself is proportional to the surface area and thickness of the capacitor, with larger and thinner capacitor surfaces providing a higher capacitance. Changes in surface area dominate a change in thickness where changes are made in all three dimensions in equal proportion. Hence, these changes do not cancel out with

increased miniaturization. Thus, miniaturization of capacitors leads to lower capacitance and thereby a shorter period between refreshes.

In addition to the relationship of capacitance with area and thickness, capacitance is also dependent upon the material used for manufacturing the capacitor. Therefore, it would be desirable to utilize materials for semiconductor capacitors which would provide larger capacitances than do the materials in present use. It would be yet more desirable to utilize such materials were they capable of further reduction in thickness.

One category of material which would provide such increased capacitance are ferroelectrics such as lead zirconate titanate (PZT) and lead lanthanum zirconate titanate (PLZT). In addition to the use of these ferroelectrics for their improved capacitance, thin film layers of these ferroelectrics on semiconductor materials could be used as active elements in a variety of thin film electro-optical devices such as optical disks, optical coatings, or optical computing logic.

Unfortunately, prior art methods do not allow for deposition of thin film ferroelectrics onto the surfaces of integrated circuits. Such prior art methods require temperatures over 500° C, while temperatures over 400° C are damaging to the integrated electronics on the integrated circuit chip. In addition to integrated circuits, there are a number of other low-temperature substrates that cannot be used with these high temperature processes.

There are additional requirements beyond temperature of the substrate which must be considered when commercially producing thin film-coated devices. Films must be conformal, which means that the film must fill in surface features. These surface features may vary from tenths of a micron to several microns in depth and lateral extent. In addition, the films themselves must have a well controlled stoichiometry, which means that the ratios of the elements comprising the ferroelectric, e.g. lead, zirconium, and titanium , and perhaps lanthanum, must be well controlled. A pure perovskite-phase material must be produced. In addition, this uniformity must be maintained over areas which may exceed areas with 8 inch diameters, and must be maintained while allowing high film growth rates.

Prior art methods such as sol-gel or rf and magnetron sputtering may be used for small scale deposition of ferroelectrics, but cannot produce conformal films over large features, and are not capable of producing a uniformly composed film over large areas with a high film growth rate. Hence, these methods appear incapable of meeting the demands of low cost commercial manufacturing of such thin film devices.

One promising method presently in use is called metalorganic chemical vapor deposition (MOCVD). In this method, a metalorganic compound is introduced into the environment surrounding the substrate material, and the substrate material is heated to a temperature which facilitates deposition of the vaporized metalorganic compound. Unfortunately, this temperature is too high for use with integrated circuit devices, as discussed above. Hence, this method also cannot achieve low temperature deposition.

There are additional benefits of lower temperature film deposition. Problems with inter-diffusion and thermal mismatch between the film and the substrate material can be minimized by low temperature coating without annealing.

Hence, it would be desirable to utilize a method of coating an integrated circuit chip with a layer of a ferroelectric material which does not require temperatures over 400° C during either deposition or annealing. Such a method should provide for a uniform conformal thin film grown over large surfaces at high growth rates.

Broadly, it is the object of the present invention to provide an improved method for depositing a thin film coating onto a substrate material that has limited temperature tolerance.

It is a further object of the present invention to provide an improved method for depositing a ferroelectric coating on a semiconductor.

It is a still further object of the present invention to provide a method of coating an integrated circuit.

These and other objects of the present invention will become apparent to those skilled in the art from the following detailed description of the invention and the accompanying drawings.

Summary of the Invention

The present invention comprises a method for coating the surface of a substrate with a thin film of ferroelectric material. A flow of a metalorganic vapor directed towards the substrate is generated. The metalorganic vapor includes precursor compounds to the ferroelectric material of the coating. Also, a flow of excited state species is generated. The flow of excited state species is directed to intersect the path of the flow of metalorganic vapor at a location displaced from the surface of the substrate. The intersection is chosen such that the metalorganic vapor and excited state species collide and produce a flow of activated metalorganic vapor. The substrate is heated to a predetermined temperature which is chosen to be less than 400^{0} C. Finally, the flow of activated metalorganic vapor is directed to collide with the surface of the heated substrate.

In the preferred implementation of the present invention the metalorganic vapor comprises a combination of tetraethyl lead, zirconium *t*-butoxide, and titanium iso-propoxide for a PZT layer, and lanthanum 2,2,6,6,-tetramethyl-3,5-heptanedionate, zirconium *t*-butoxide, and titanium iso-propoxide for a PLZT layer. Also, the flow of ionized particles comprises a flow of ionized helium, and is directed by means of a pressurized gas flow. The step of generating a flow of ionized particles comprises the step of directing a plasma gas flow towards the silicon substrate and through a radio frequency electromagnetic field of sufficient field intensity to ionize the plasma gas.

The method of the present invention may also be used to produce thin film coatings of a variety of other materials to the surface of an integrated circuit device.

Brief Description f the Drawings

Figure 1 illustrates a PE-MOCVD reactor in which the preferred implementation of the method of the present invention may be performed.

Detailed Description of the Invention

The method of the present invention may be described as a Plasma Enhanced Metalorganic Chemical Vapor Deposition (PE-MOCVD) method. This is an improvement to the MOCVD method described above. By utilizing excited state species generated in a plasma to activate the metalorganic precursor vapor, more effective deposition may be achieved and lower substrate temperatures are possible. The excited state species are directed to a location spatially removed from the substrate surface, where the excited state species interact with the metalorganic precursor vapor. It is important to have the interaction at a point removed from the substrate since locating a substrate within the particle flow can lead to serious problems such as film and substrate damage from high energy electron and ion bombardment, lack of control over the chemical environment at the film growth surface, and gas phase particle nucleation from precursors entering the discharge. These problems are avoided by the displacement of the location of the excited state species-precursor interaction from the plasma generation zone.

The manner in which the present invention provides its advantages is best understood by first considering the PE-MOCVD reactor of Figure 1. The reactor includes four major sections. The first, a plasma generation chamber 10, is utilized to generate a gas of excited state species. The excited state species comprise non-izoned atoms in excited states. The second is a precursor activation chamber 20, in which the excited state species are utilized to activate a flow of precursor vapor to render the precursor vapor more susceptible to successful deposition upon the surface of substrate 32. The third is the film growth chamber, in which the substrate 32 is heated by a heater 36 and is bombarded with activated precursor vapor. The combination of activated precursor vapor with the heated substrate surface yields more effective deposition of film material. Finally, a vacuum exhaust system 40 generates a low pressure region which draws residual activated precursor vapor and discharges the vapor. The vacuum thereby produced is essential to the proper flow of gasses within the reactor.

The preferred implementation of the method may be best understood in terms of the operation of the PE-MOCVD reactor outlined above. A flow of a precursor vapor is generated by precursor vapor injectors 22. This flow is directed

towards the substrate 32. The flow can be adjusted by changing the relative positions of precursor vapor injectors 22 and substrate holder 34. Precursor vapor injectors 22 may be moved relative to film growth chamber 30 and substrate holder 34 may be manipulated by moving substrate manipulator 46. In alternative implementations of the method of the present invention secondary activating species may be introduced with the precursor vapor to facilitate activation and film deposition.

A flow of ionized particles is produced by discharging a plasma gas into plasma generation chamber 10 by means of plasma gas inlets 12. The plasma gas is set into motion by means of a flow generated by vacuum exhaust system 40, which creates a pressure difference which induces the flow. As the plasma gas flows through the section of plasma generation chamber 10 contained within rf coil 14, it passes through plasma generation zone 18. A radio-frequency electromagnetic field is generated by rf coil 14 which causes the plasma gas to ionize, thereby generating a plasma. This plasma is therefore a flow of ionized particles.

The plasma flows towards substrate 32. Along the path of the flow of ionized particles a buffer gas may be introduced at buffer inlets 16. The buffer gas facilitates plasma transport and activation of the precursor vapor, as described below.

The afterglow of the plasma continues to flow into precursor activation zone 20. Precursor activation zone 20 is displaced from plasma generation chamber 10 by a sufficient distance to allow substantially all of the ionized particles in the plasma to decay to excited state species. The afterglow is directed by the vacuum to flow so as to intersect the path of the flow of precursor compound vapor in precursor activation zone 20. Precursor activation zone 20 is displaced from the surface of substrate 32. The two flows intersect such that the precursor vapor and excited state species particles in the plasma afterglow collide. The excited state species particles interact with the precursor vapor, transforming the precursor compound into an "activated" precursor vapor. This process therefore results in the production of a flow of activated precursor vapor. Also, a buffer gas may be introduced at buffer inlets 16. The buffer gas facilitates plasma transport and activation of the precursor vapor.

In order to facilitate adhesion of the activated precursor compound to the surface of substrate 32, substrate 32 is heated to a predetermined temperature by means of heater 36 and thermocouple 38. For integrated circuit devices, this predetermined temperature is chosen to be less than 400° C. The specific temperature chosen is dependent upon the maximum temperature to which the substrate may be heated without damage thereto. Hence, the temperature is dependent upon the substrate material itself.

Finally, the flow of activated precursor vapor is directed to collide with the surface of substrate 32. The locations of substrate holder 34 and precursor vapor injectors 22 may be adjusted so that the flow is properly directed towards substrate 32, as mentioned above.

In one preferred implementation of the present invention, a thin film of a ferroelectric material is deposited onto a silicon surface. In particular, either of a PZT or a PLZT, is to be deposited. In such a case the precursor vapor is comprised of a combination of metalorganic compounds, which preferably are tetraethyl lead, zirconium *t*-butoxide, and titanium iso-propoxide for PZT films and tetraethyl lead, lanthanum 2,2,6,6,-tetramethyl-3,5-heptanedionate, zirconium *t*-butoxide, and titanium iso-propoxide for PLZT films. Other precursor compounds may be substituted, dependent upon the film material sought to be deposited.

The flow of plasma in the preferred implementation comprises a flow of ionized helium. The plasma is generated by passing a 13.56 MHz rf voltage through rf coil 14. The buffer gas is also helium gas. Alternative gasses may be used, as will be obvious to those skilled in the art.

It is important to note that the gas pressures at the various locations within the reactor are critical to its operation. The pressure differentials between plasma gas inlets 12, plasma generation zone 18, and precursor activation zone 20 must be such that a continuous gas and plasma flow is achieved, and that precursor vapor does not flow into plasma generation zone 18. The gas pressures are maintained by regulating vacuum exhaust system 40, buffer inlets 16, plasma gas inlets 12 and precursor vapor injectors 22 in a standard feedback control loop.

In the preferred implementation, monitoring and control devices (not shown) are utilized in the regulatory feedback loop. A capacitance manometer and a controller are included. Exhaust system 40 would include an exhaust throttle valve. A metering valve may be included on buffer inlets 16. Plasma gas inlets 12 and buffer inlets 16 may have gas flow rates regulated by mass flow controllers. Precursor vapor injectors 22 may be regulated by metered carrier gas flows through heated bubbler tubes or by means of pressure controlled vapor metering valves. The specific regulation devices may be chosen in light of the precursor compounds and plasma gas utilized.

The method of the present invention has been described herein in terms of the preferred implementation using the PE-MOCVD reactor described above. Alternative embodiments will become obvious to those skilled in the art. By way of example, alternative plasma generation methods may be utilized, such as static or microwave field stimulation or electron-cyclotron resonance (ECR) contained discharge. Also, plasma flow may be facilitated and regulated by means of electromagnetic fields.

There has been described herein a method for coating a semiconductor surface with a thin film. Various modifications to the present invention will become obvious to those skilled in the art from the foregoing description and accompanying drawings. Accordingly, the present invention is to be limited solely by the scope of the following claims.

WHAT IS CLAIMED IS:

1. A method for coating the surface of a substrate with a thin film of ferroelectric material, said method comprising the steps of: generating a flow of a metalorganic vapor directed towards said substrate, said metalorganic vapor comprising a combination of precursor compounds to said ferroelectric material to be deposited; generating a flow of excited state species; directing said flow of excited state species to intersect the path of the flow of metalorganic vapor at a location displaced from said surface of said substrate, the intersection being such that said metalorganic vapor and excited state species collide and produce a flow of activated metalorganic vapor; heating said substrate to a predetermined temperature; and directing said flow of activated metalorganic vapor to collide with said surface of said heated substrate.

2. The method of Claim 1 wherein said predetermined temperature is less than 400° C.

3. The method of Claim 1 wherein said precursor compounds comprise among tetraethyl lead, zirconium *t*-butoxide, and titanium iso-propoxide.

4. The method of Claim 3 wherein the precursor compounds further comprise lanthanum 2,2,6,6,-tetramethyl-3,5-heptanedionate.

5. The method of Claim 1 wherein said step of generating a flow of excited state species comprises generating a flow of ionized Helium.

6. The method of Claim 1 wherein the flow of excited state species is directed by means of a pressurized gas flow.

7. The method of Claim 1 wherein said step of generating a flow of excited state species comprises the step of directing a plasma gas flow towards said substrate and through a radio frequency electromagnetic field of sufficient field intensity to ionize said plasma gas.

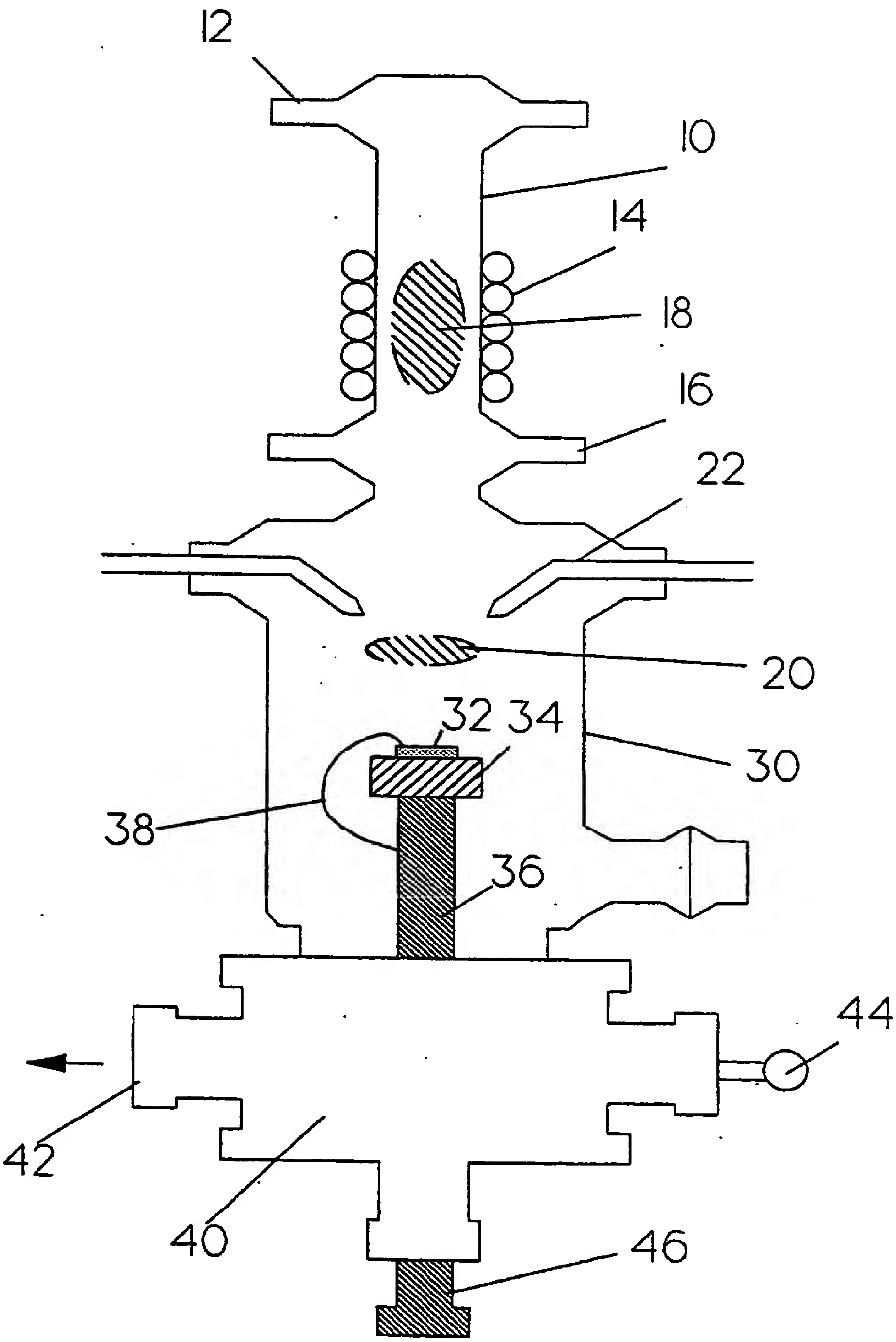

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/00259

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B05D 3/06; C23C 16/02,16/22,16/46,16/50
US CL :427/255.1,255.13,126.3,226,561,562,566
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/255.1, 255.13, 126.3, 226, 561, 562, 566

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS-PZT,PLZT, ferroelectric#,plasma, remote plasma, vapor deposition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P Y	US,A, 5,138,520 (MCMILLAN ET AL) 11 AUGUST 1992 See col. 1, lines 9-18,29-40	1,6-7 2-5
Y,P	US,A, 5,104,690 (GREENWALD) 14 APRIL 1992 See col. 2, lines 33-34	2-5
Y,P	US,A, 5,116,643 (MILLER ET AL) 26 MAY 1992 See col. 5, lines 9-10	2-5
A	US,A, 4,963,390 (LIPELES ET AL) 16 OCTOBER 1990 See abstract	1-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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